電気材料技術雑誌 第14巻第2号
J.Soc.Elect.Mat.Eng. Vol.14, No.2, 2005

Rechargeable Battery with an Organic Radical Polymer

Masaharu Satoh, Kentaro Nakahara, Jiro Iriyama, Shigeyuki Iwasa,
and Masahiro Suguro
Fundamental and Environmental Research Laboratories, NEC Corporation
34 Miyukigaokam Tsukuba-shi, Ibaraki 305-8501, Japan
Tel: +81-29-850-1556, Fax: +81-29-850-2635
E-mail: m-satoh@ap.jp.nec.com

As transmission signal volumes of various information systems rapidly increase and broadband technology progresses, electronics devices have been required a breakthrough to overcome the conventional limitations becoming part of the sophisticated makeup of next-generation applications. It is generally accepted that the development of new material often leads to epoch-making innovation. So far, we have developed a new capacitor with an excellent performance utilizing conducting polymer as a counter electrode of solid electrolyte tantalum capacitor (NEOCAPACITOR, 1994). Replacement of a conventional counter electrode by highly conductive polymer causes a capacitor with small inner resistance, which means a increased current allowance and extended accessible frequency range of the capacitor that correspond to the high-speed electronic device[1,2]. The capacitor is used for most of the advanced information apparatuses such as mobile phone and personal computer.

Organic radical polymers should be a next example of the epoch-making innovative material. These polymers have been used as one-dimensional throw-bond organic ferromagnets, and considerable effort has been made to increase their values of spin quantum number in an electronic ground state. In addition to that, many radical polymers are known to be oxidized and reduced electrochemically without producing the highly reactive species like radical-cation or radical-anion. For example, stable nitroxide radical displayed a reversible redox reaction between the corresponding oxo-ammonium salt. These redox processes would be suitable for a reaction of cathode active materials in rechargeable battery [3, 4].

Here we describe the electrochemical properties and the performance of the of a stable nitroxyl polyradical, poly (2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA), prototype lithium battery using this design. Because of a smooth and fast electrochemical redox reaction for the PTMA cathode (Fig.1), Organic radical battery, ORB is able to charge and discharge with high current density. Using cyclic voltammetry, we have confirmed that this polyradical demonstrates a reversible redox wave and is thus suitable for use as the cathode active material in a secondary battery. ORB based on the electrochemical redox reaction of PTMA should be promising as quick chargeable and high power density battery.

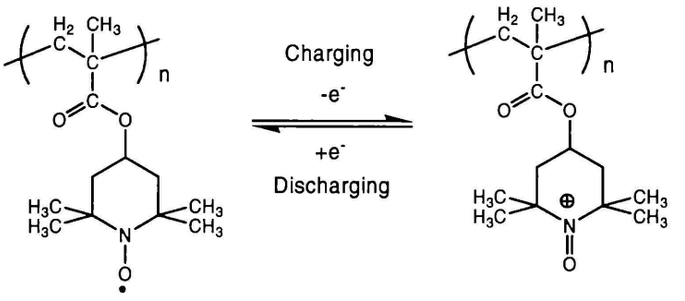

Fig. 1. Charging and discharging process of PTMA cathode.

ORB cells were fabricated with the modified method of a lithium-ion battery [5]. Both lithium metal and a graphite intercalation compound were applied as anode active materials for the organic radical battery. Carbonate into which lithium salt had been dissolved was used as the electrolyte solution.

A half-wave potential ($E_{1/2}$) of PTMA is 3.58 V vs. Li/Li^+. It is noted that the difference of ration of the anodic and cathodic peak potentials is estimated as 0.16 V at a sweep rate of 10 mV/sec, which is extremely smaller than that of the other electro-active organic materials such as conducting polymer and disulfide compounds. The small gap of the anodic and cathodic peaks corresponds with its fast electrode reaction rate of the polyradical, which leads to a capability for high power rate in the charge and discharge process of the battery.

Figure 2 and 3 show the charge and discharge profiles of coin type ORB cells (PTMA cathode/Li anode). In these figures, C is a value indicating current and expressed as a multiple of nominal capacity. It is clearly observed that the cell demonstrates sufficiently high capacity at extremely higher charging and discharging rates. That is, ORB is enables to charge up to 80% within 1 minute (60C). The small decline in both charging and discharging curves indicates that the rate limitation process of the cell does not depend on the reaction rate of PTMA.

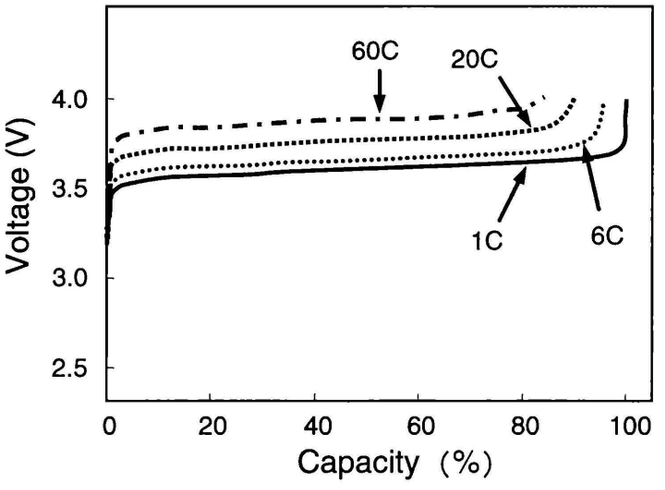

Fig. 2. Charge profiles of ORB cell (PTMA cathode/Li anode) at various rates.

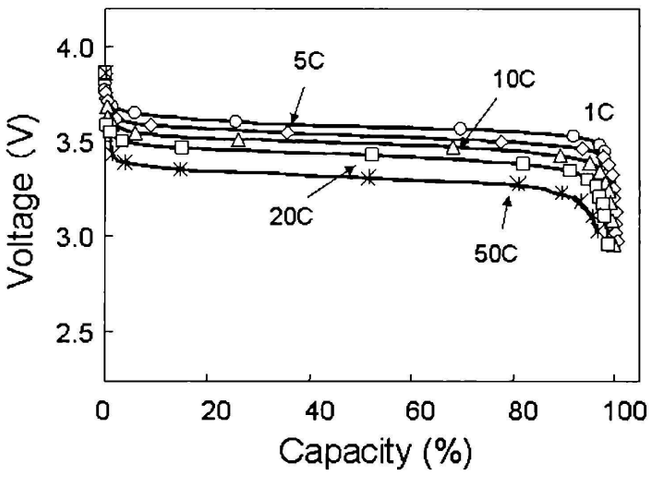

Fig. 3. Discharge profiles of coin type ORB cell (PTMA cathode/Li anode) at various rates.

To demonstrate practical application of the ORB, we fabricated a 100-mAh class film-packed cell (size: 55×43 mm excluding the sealing region, thickness 4 mm) with PTMA cathode and Graphite anode. The outer view of a film packed ORB under development is shown in Fig. 4. The cell is able to discharge over 10 A for a cut-off voltage on 2.5 V with excellent efficiency and cycleability.

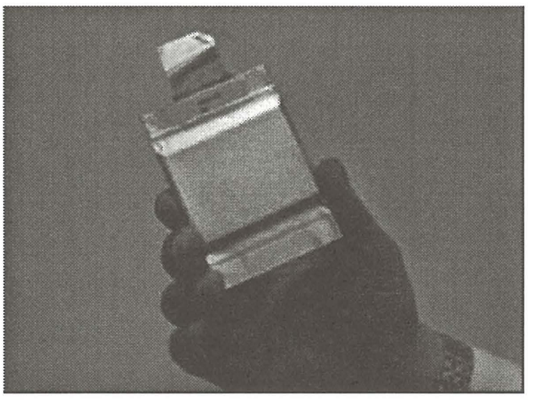

Fig. 4. Photo of 100mAh-class ORB cell (PTMA cathode/Graphite anode)

The measured power density, 10 kW/kg, indicates that the cell is capable of driving a various information systems such as desktop PC and PDAs. Fig. 5 shows the position of ORB in ragone plots. It is apparently observed that the ORB transcends the limitation of conventional energy devices. The quick chargeable and high power ORB opens up a new field of high power density, environmentally

friendly batteries. That is, ORB can be charged whenever and wherever necessary. The ORB should be promising a key device for the next ubiquitous society.

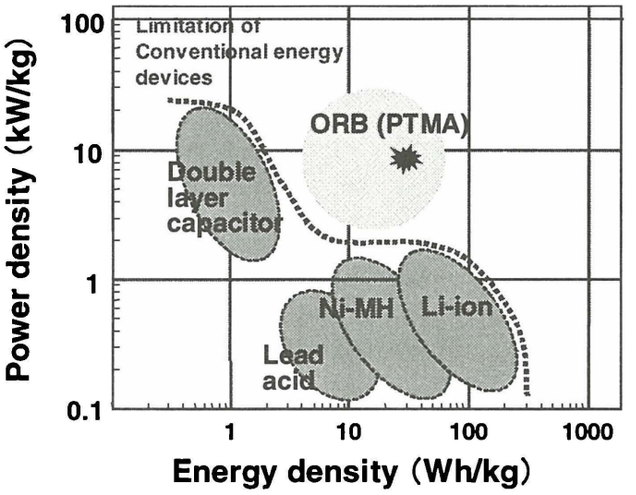

Fig.5 Position of ORB and other energy devices in Ragone plots.

Acknowledgments

This work was performed as part of the high power density organic radical battery project for data-backup and was supported by the New Energy and Industrial Technology Development Organization (NEDO)

References

[1] M. Satoh, H. Ishikawa, K. Amano, E. Hasegawa, and K. Yoshino, *Synth. Met.*, **65** (1994) 39.

[2] M. Satoh, H. Ishikawa, K. Amano, E. Hasegawa, and K. Yoshino, *Synth. Met.*, **71** (1994) 2259.

[3] K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro and E. Hasegawa, *Chem. Phys. Lett.*, **359** (2002) 351.

[4] K. Nakahara, J. Iriyama, S. Iwasa, M. Suguro and M. Satoh, *207th ECS, Meeting Quebec*, **188** (2005).

[5] M. Satoh, K. Nakahara, J. Iriyama, S. Iwasa, and M. Suguro, *IEICE Trans. Electron.*, **Vol.E87 C**, No.12, (2002) 2076.